Direct Measurement of Mercury Reactions in Coal Power Plant Plumes

Initial Coordination Meeting for the Department of Energy
National Energy Technology Laboratory

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List of 5 SPDC Study Locations to Date

- October 2002 at Plant Bowen, EPRI (Levin), Southern Company, (Jansen), in collaboration with TVA (Valente) and EERC (Laudal and Schulz)
- March 2000 @ EERC UARG-EPRI (Michaud and Levin), CATM-EERC (Laudal), EPA-ORD (Kilgroe) and FGS (Prestbo)
- May 1997 @ Dickerson and Mont. Co. Waste Inc. Maryland DNR-PPRP (Sherwell) and ERM (J. Ross)
- February 1995 @ WEPCO-PIPP Wisconsin DNR (Knauer) and EPA GLNPO(A. Bandemier)

Overarching scientific question: Does the speciation of mercury change significantly from flue to the plume?

Specific Scientific Questions for Mercury Plume Chemistry

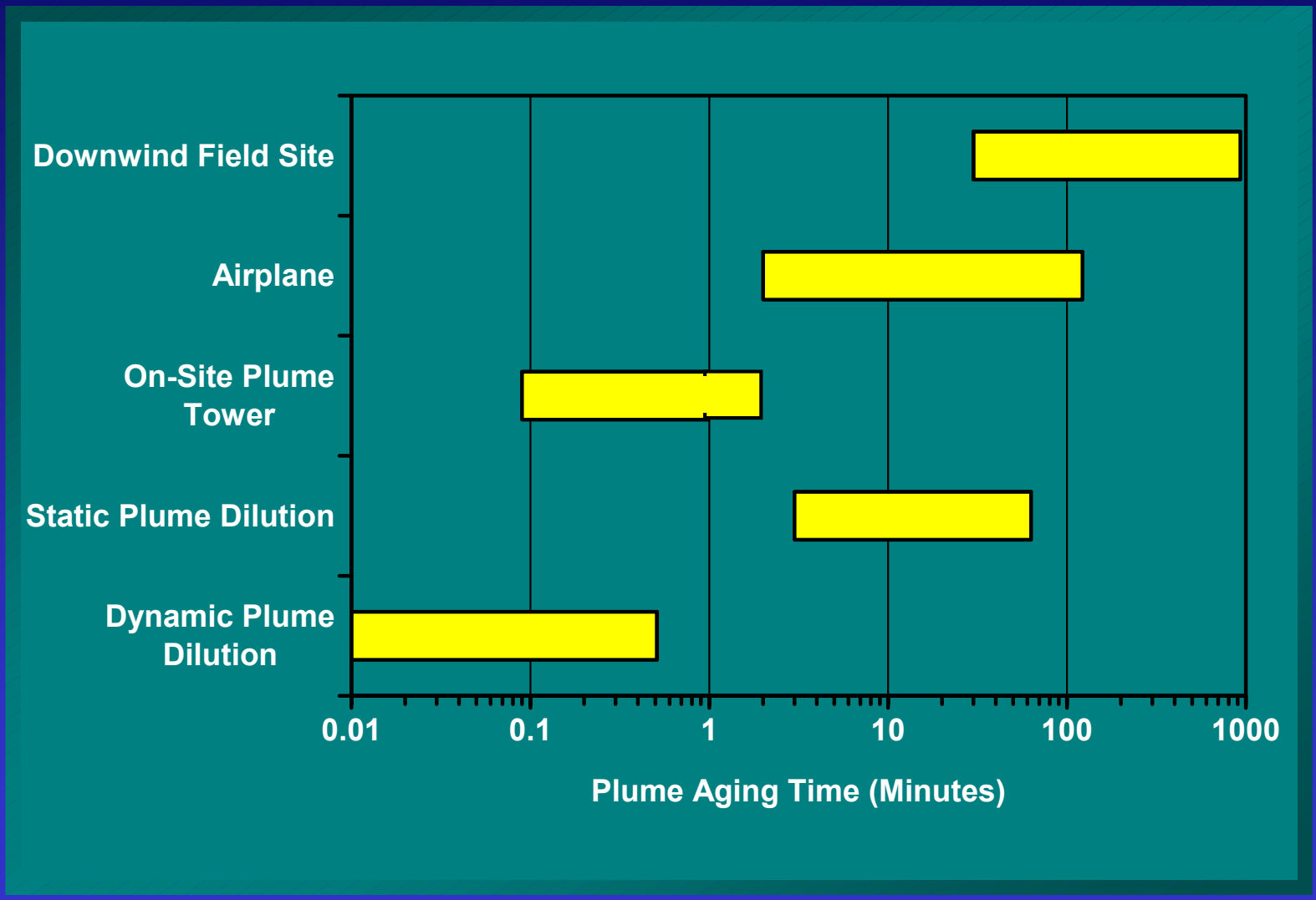
- Is there any important mercury chemistry occurring at the initial mixing of flue gas with ambient air?
- Do gas phase Hg(II) species dry deposit to surfaces and how fast?
- Are the gas-phase Hg(II) species readily washed out during the addition of simulated rain?
- Does gas-phase Hg(II) adsorb to particulate matter as observed in the TVA Paradise Plume Study

How can we study Hg plume chemistry?

- Paradigm 1 – measure reaction rates in lab – apply in model
- Paradigm 2 – Conduct observational studies where there are big data gaps to provide feedback, challenge assumptions and direct future research.
- For example: TVA Paradise Plume Study – nearly all the Hg(II) reported to particulate in the plume – this was justification for speciation profile that EPA used in the RELMAP model of 20% particulate for coal Hg sources.
- Both approaches will contribute to the improvement and accuracy of atmospheric models -- which is one of our primary tools used to help determine fate and effects.

Plume Study Options:

Important to understand the boundaries of past and future studies

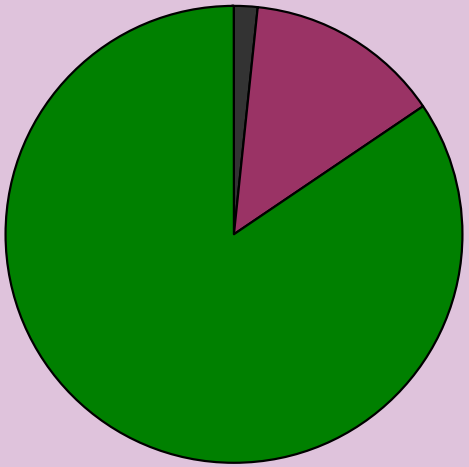


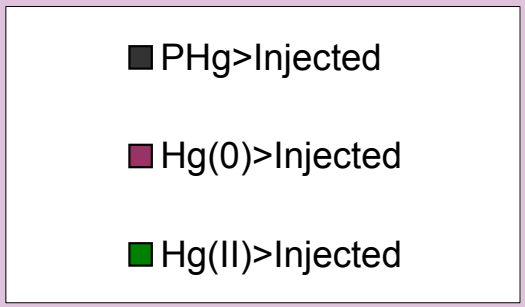
Justification for further SPDC experiments supported by aircraft and dynamic dilution methods

- SPDC EERC Study – Enrichment of Hg^0 in the plume
- The amount of plume Hg^0 is greater than the amount injected into the SPDC – suggesting a conversion of Hg(II) to Hg^0.
- The conversion is fast (<4 minutes) and significant in magnitude
- For SPDC runs with the ESP (higher particulates) the Hg^0 increase averages a factor of 3.8 ± 1.5
- For SPDC runs with the baghouse (lower particulates) the Hg^0 increase averages a factor of 1.7 ± 0.94

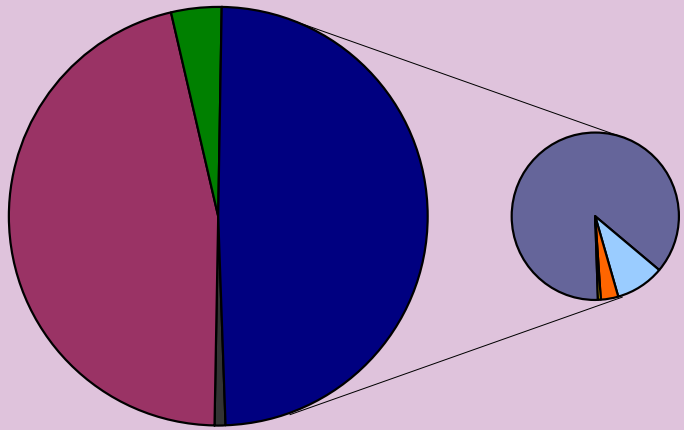
Example of Hg^0 Conversion for Note Increase in Hg^0 in Maroon Color

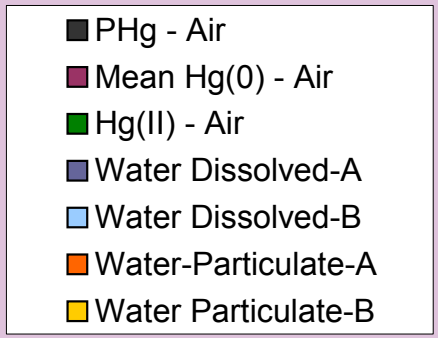
Expected SPDC Hg Concentration
SPDC Run 0313-6
Blacksville - ESP - Hg^0+Hg(II) spike
nightime-no rain





Measured SPDC Hg Concentration
Mass Balance (measured/expected) = 1.08

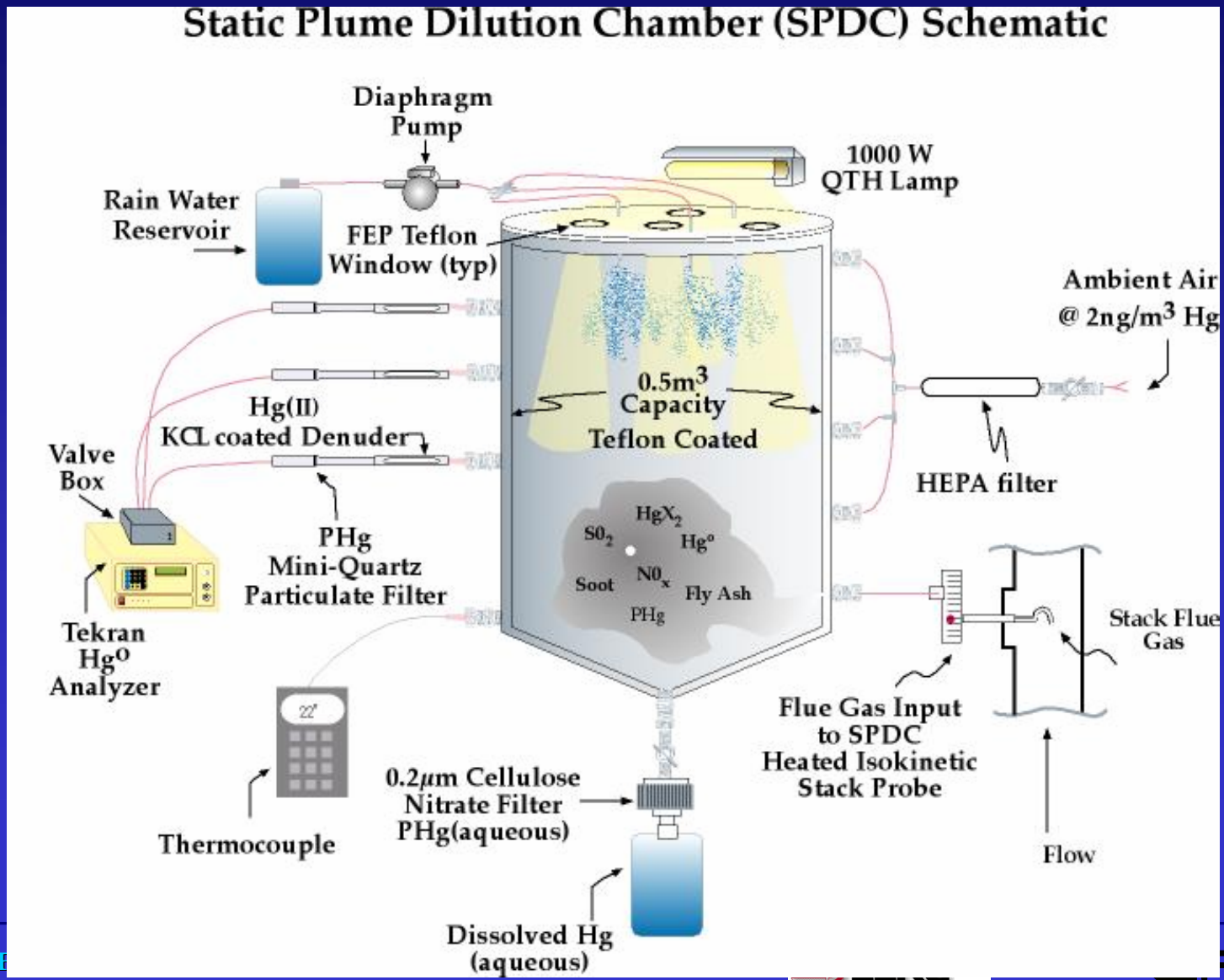




Coal Plume Hg Chemistry Comments

- Conversion of Hg(II) → Hg^0 not surprising considering the reactivity of the flue gas matrix and observations of $HgCl_2$ > Hg^0 in the laboratory
- This Hg(II) to Hg^0 conversion has been observed in 3 different power plants, 2 different SPDC devices and at various dilution ratios.
- Conversion is too fast to be observed by the SPDC
- Initial results of the ground-based SEARCH program to measure downwind plume chemistry supports SPDC observation of Hg(II) → Hg^0

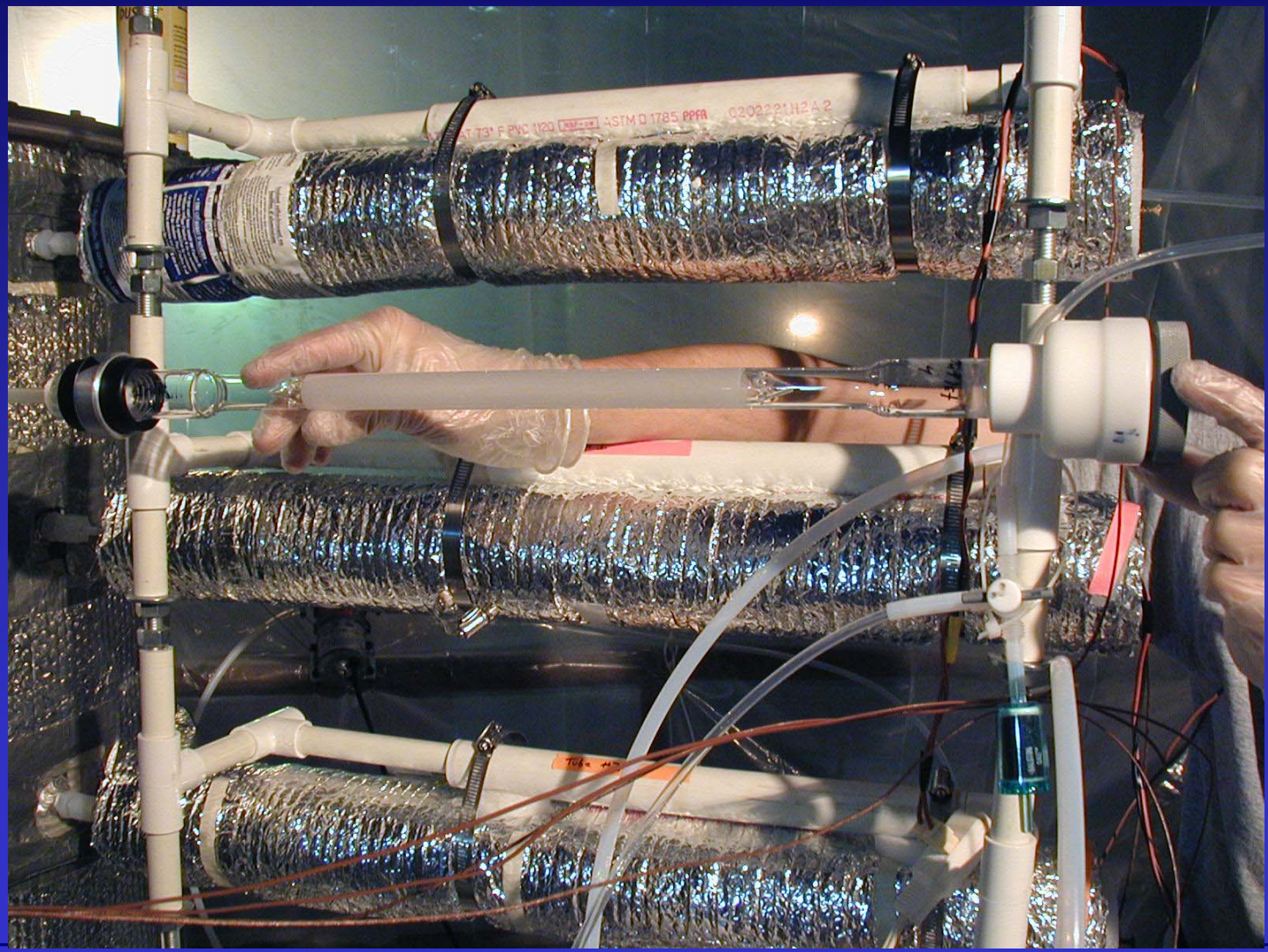
How will we do the plume study Animation of SPDC Analytical Technique



Brief SPDC Method Description

1. Fluegas Input Speciation known via Ontario Hydro and Hg-CEM Measurements (EERC) and FMSS Method (Frontier).
2. Input known volume of flue gas into the SPDC (2-5 liters) and dilute immediately with filtered ambient air
3. In SPDC, gas phase Hg^0 measured continuously with Tekran.
4. Hg(II) and PHg measured directly after dilution as 3 x 2.5 min. discrete samples
5. Dry deposited Hg(II) and PHg recovered by wall wash with pH 4.8 simulated rain water
6. Data Interpretation focuses on the comparison of measured flue gas speciation with measured SPDC speciation – How does it change from duct to plume??

SPDC Speciation Sample Train (based on Landis et al., ES&T, 2002)

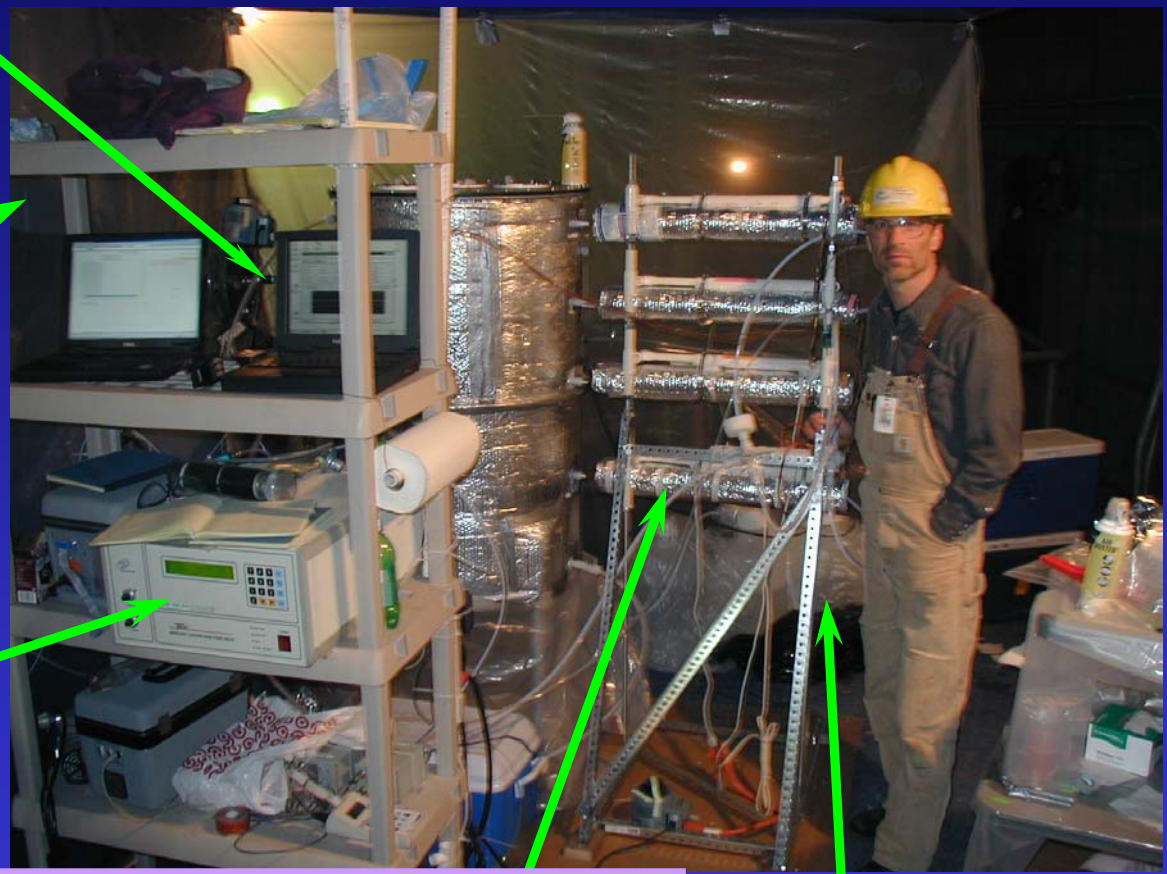


SPDC at Plant Bowen

Duct to SPDC Interface

Flue gas Duct

Tekran Real-Time Hg^0



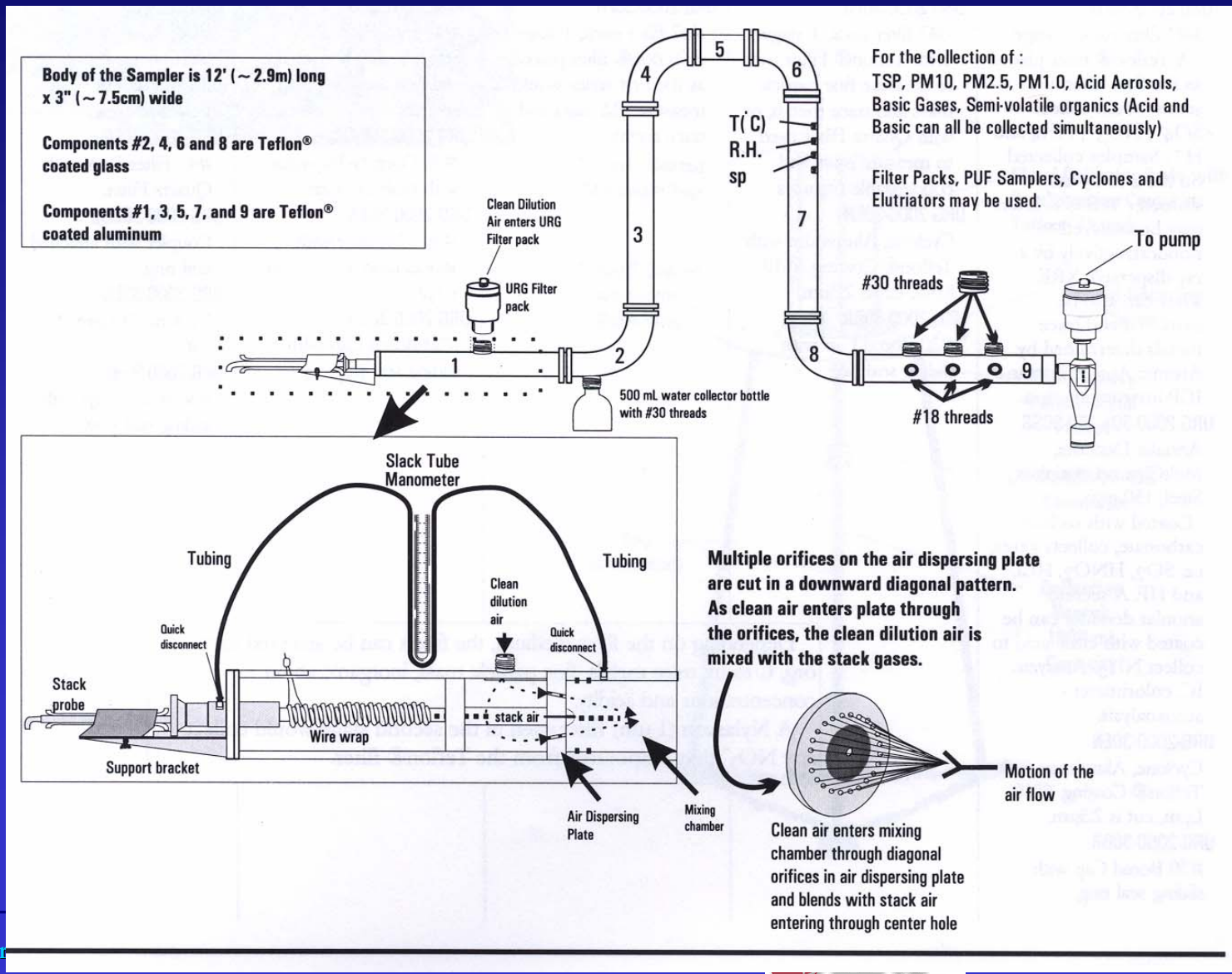
SPDC Spectiation Denuder/Filter System

Rainwater Wash System

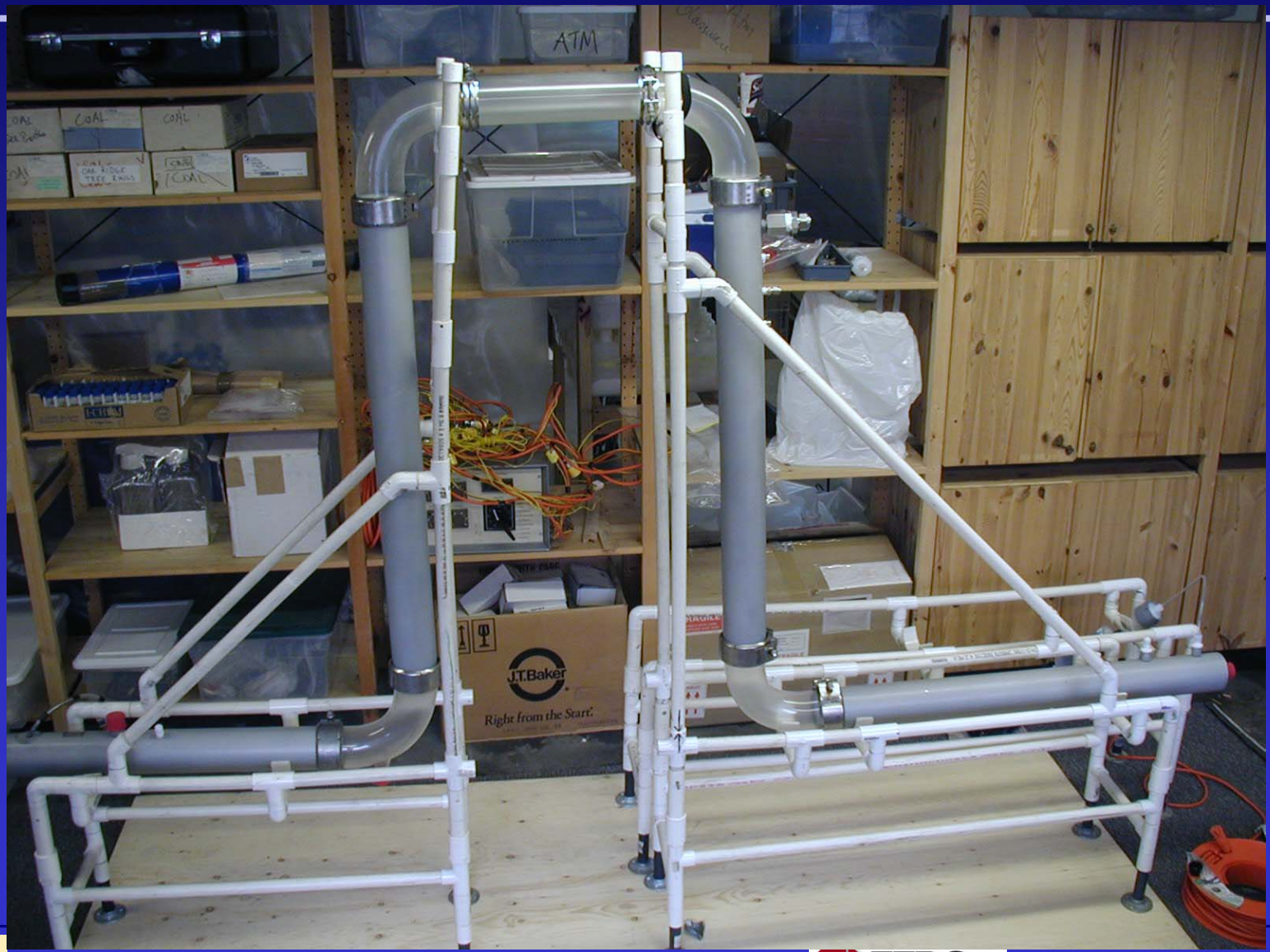
Justification for Application of the Dynamic Plume Dilution Method

- It has been observed that the potential conversion of gaseous Hg(II) to Hg^0 is faster than the SPDC can observe (<1 minute).
- The Dynamic Plume Dilution (DPD) method is necessary to capture the mercury speciation in the 5 to 30 second reaction time frame.
- The DPD, unlike the SPDC has the capability to easily change the flue gas dilution ratio and reaction time during the course of a sample run while observations of Hg^0 are being made.

Dynamic Dilution to Simulate Plume Chemistry and Determine Effective Reaction Rates



Dynamic Plume Dilution Unit



Possible Problems and Solutions

- SPDC method is now "routine" and reliable.
- Tekran is our workhorse for the SPDC monitoring – backup lamps, cartridges, fittings and FedEx will cure most problems
- Logistics of simultaneous airplane, stack monitoring and SPDC solved through continuous updates via cell-phones and 2-way radios
- Dynamic plume dilution method is untested in the field – crux of the problem is getting an accurate dilution ratio and quantifying wall losses.